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DETERMINATION OF PENTOSANS IN PULPS AND PAPERS

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ABSTRACT

A relatively rapid method for the determination of pentosans in pulps and papers is described. A simple volumetric procedure was adapted to the analysis of the distillates for furfural. With minor changes, the simple method of distillation prescribed by the Association of Official Agricultural Chemists was retained, since a comparison, using a variety of pulps, showed that various other methods gave no higher yields of furfural. For example, distillation in a current of steam from hydrochloric acid nearly saturated with ammonium chloride greatly increased the yield of volatile material, perhaps hydroxymethylfurfural, from cellulose, but not of furfural from pentosans. The error due to volatile material other than furfural in the AOAC distillates was found to be 0.9 percent, in terms of pentosan, for all of the usual wood pulps. This correction was determined by two independent methods, namely, fractionation of the distillates by redistillation, and study of the rates of evolution of volatile material. Experiments also showed that the volatile material from a typical cotton fiber arose mainly from substances other than pentosans.

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I. INTRODUCTION

The method generally used ¹ for the estimation of pentosans specifies distillation of the material with 12-percent hydrochloric acid until 360 ml is collected in 120 minutes. The furfural in the distillate is then precipitated and weighed as the phloroglucide, from which the weight of the pentosan is calculated, using Kröber's tables. Ordinary distilling apparatus, with water-cooled condenser, is used. A separatory funnel mounted above the distilling flask contains the acid which is added in portions during the distillation. This arrangement, with the simple modification of attaching the receiver to the end of the condenser by means of an adapter and rubber stoppers, will be referred to subsequently as the "simple" distilling apparatus.

Both the distillation and the furfural determination have been the subject of much study. Pervier and Gortner,² among others, have

¹ Official and Tentative Methods of the Association of Official Agricultural Chemists, p. 344 (1935). See also *Methods used at the Forest Products Laboratory*, Paper Trade J. 87, 67 (December 20, 1928).

² N. C. Pervier and R. A. Gortner, *Ind. Eng. Chem.* 15, 1169, 1255 (1923). This contains a bibliography and a rather comprehensive discussion of the subject.

suggested that furfural may be partially decomposed by the hot hydrochloric acid under the conditions of the distillation, and therefore, that the furfural should be removed as quickly as possible by a current of steam. Kullgren and Tyden³ found a 3-percent loss in attempting to recover known quantities of furfural by distilling from hydrochloric acid saturated with sodium chloride to salt out the furfural. Kline and Acree⁴ found no essential difference between the results of steam and simple distillation. Recently, Hughes and Acree⁵ reported quantitative conversion of xylose to furfural by distilling in a current of steam from hydrochloric acid saturated with sodium chloride.

Much of the work on the development of a method for determining pentosans has been rendered difficult of interpretation owing to the lack of a sufficiently simple and accurate method for estimating furfural. The use of phloroglucinol and other precipitants has many disadvantages other than those usually associated with gravimetric methods.^{3,4} Of the volumetric methods proposed, that used by Powell and Whittaker,⁶ with the modification by Hughes and Acree,⁷ appears to be the simplest and most accurate. In this method a known excess of potassium bromate-bromide is added to the cold (0 to 2° C) furfural-hydrochloric acid solution in a special side-arm flask and the liberated bromine allowed to react for 5 minutes, after which the unused bromine is determined iodometrically. With this method the last-named authors were able to determine furfural within 0.35 percent, on an average, of the known amount.

Various workers, especially Kullgren and Tyden, have shown that volatile compounds other than furfural, for example, hydroxymethylfurfural from hexoses, may be present in distillates from wood pulps. Cunningham and Doree⁸ report that the amounts of furfural and hydroxymethylfurfural obtainable from cotton may be varied by previous chemical treatments, their results being based upon the difference in solubilities of the phloroglucides.

The present work was undertaken to adapt, if possible, the results of recent developments in the furfural determination and in the distillation procedure to a simple and relatively accurate method for the determination of pentosans in pulps and papers. Steam distillation with ammonium chloride, which is much more soluble than sodium chloride in hot hydrochloric acid, and therefore may be more effective for salting out the volatile products, was investigated for possible increased yields of furfural from pentosans. An effort, furthermore, was made to determine the amount of volatile material arising from cellulose during the pentosan distillation, and to arrive at a value for the correction which would be generally applicable in determinations of pentosans in pulps and papers.

³ C. Kullgren and H. Tyden, *Ing. Vetenskaps Akad., Handl.* **94**, 3-62 (1929).

⁴ G. M. Kline and S. F. Acree, *BS J. Research* **8**, 25 (1932) RP398.

⁵ Elizabeth E. Hughes and S. F. Acree, *J. Research NBS* **21**, 329 (1938) RP1132.

⁶ W. J. Powell and H. J. Whittaker, *J. Soc. Chem. Ind.* **43**, 35T (1924).

⁷ Elizabeth E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.* **6**, 123 (1934).

⁸ M. Cunningham and C. Doree, *Biochem. J.* **8**, 445 (1914).

II. EXPERIMENTAL RESULTS AND DISCUSSION

1. DETERMINATION OF FURFURAL

Known quantities of a standard aqueous solution of furfural⁹ were added to a solution of hydrochloric acid in 1-liter glass-stoppered reagent bottles, to make 350 ml of a solution, 2.7 *N* in HCl.¹⁰ Two hundred and fifty g of crushed ice was added and after the temperature had fallen to -2° to 0° C, 20.00 ml of a 0.2 *N* solution of potassium bromate, containing 50 g of potassium bromide per liter, was added. The bottles were then closed and the contents thoroughly mixed. After 5 minutes, 10 ml of a 10-percent solution of potassium iodide was added. After the remaining bromine had been completely absorbed, the liberated iodine was titrated with thiosulfate using starch indicator. Representative results are given in table 1, series 1 to 4. Series 5 is presented to show that essentially the same value for the amount of furfural in 20.00 ml of standard solution was obtained, using either ordinary reagent bottles or special sidearm flasks¹¹ in the determination.

TABLE 1.—Determination of furfural

Series	Bromine used: in terms of 0.00931 <i>N</i> thio- sulfate solution	Furfural found	Deviations from known value
	<i>Milliliters</i>	<i>Grams</i>	<i>Percent</i>
1. 25 ml of furfural solution=0.1250 g.....	26.24 26.27 26.29	0.1251 .1252 .1253	0.1 .2 .2
Average.....		0.1252	0.2
2. 20 ml of furfural solution=0.09997 g.....	21.00 21.01 21.01	0.1001 .1001 .1001	0.1 .1 .1
Average.....		0.1001	0.1
3. 10 ml of furfural solution=0.04998 g.....	10.47 10.47 10.53	0.04991 .04991 .05019	-0.1 -.1 .4
Average.....		0.05000	0.1
4. 5 ml of furfural solution=0.02499 g.....	5.23 5.25 5.23	0.02493 .02503 .02493	-0.2 .1 -.2
Average.....		0.02496	-0.1
5. 20 ml of furfural solution=0.0997 g. (Special flask used.)..	20.92 21.01 20.94	0.09972 .1001 .09982	-0.2 .1 -.2
Average.....		0.09988	-0.1

⁹ The furfural was distilled under reduced pressure, 190 mm, at 118° C, to obtain an almost water-white product. From the middle one-third fraction 9.997 g was then weighed out for 2 liters of solution. The amount of furfural lost by volatilization during the weighing was found to be 0.3 mg.

¹⁰ The usual concentration of acid in the pentosan distillates in the procedure to be described is 2.7 *N* after dilution. Further dilution by the melting ice and by the reagents added usually reduces the acidity to 1.3 *N* when the solutions are ready for titration with thiosulfate.

¹¹ Elizabeth E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.* **6**, 292 (1934). These flasks have two sidearms to contain the bromate and iodide so that these reagents may be added without opening the flasks at the risk of losing bromine. Very little bromine is lost when the 1-liter glass-stoppered reagent bottles are used, however, provided that the stopper is replaced without delay after addition of the iodide. Experiments in which 20.00 ml of bromate-bromide solution was titrated under test conditions in both the side-arm flasks and the reagent bottles showed the average volumes 40.72 and 40.66 ml, respectively, of 0.1 *N* thiosulfate solution necessary. This loss, corresponding to 0.15 percent of bromine, results in an error which is smaller than the average deviation in table 1, provided that the blank is determined under test conditions.

The use of crushed ice makes it possible to cool very quickly to 0° to -2° C. This temperature interval appears especially favorable for limiting the reaction between furfural and bromine to a molar ratio of 1:1. The quantities of reagents used make the method applicable to the analysis of the ordinary pulps and papers without the necessity of taking aliquot portions.

It is to be noted that the precision shown in table 1 is actually much higher than is required for a pentosan method, inasmuch as an error of 0.1 percent in the amount of furfural corresponds to an error of 0.01 percent in the pentosan content of a material containing 10 percent of pentosans.

2. COMPARISON OF METHODS OF DISTILLATION, USING PULPS AND PAPERS CONTAINING PENTOSANS

In order to compare the results obtained by simple distillation with those obtained by distilling in a current of steam from hydrochloric acid saturated with sodium chloride, the latter to be referred to subsequently as "distillation with NaCl+steam," the simple distilling apparatus was used with certain changes. The 1-liter reagent bottles serving as receivers were connected by means of an adapter and rubber stoppers to the end of the condenser, thus forming a closed system, except for a small U-trap¹² containing 5 ml of water and glass beads, which was mounted in the rubber stopper of the receiver. In addition to this, for the distillations with steam, a glass tube drawn out to a small diameter projected 1 cm below the surface of the liquid in the distilling flask, and admitted the steam from a large flask of boiling distilled water. Twenty grams of sodium chloride was added to the distilling flask.

In the simple distillation, 1 g of pulp or paper was added to 100 ml of 12-percent (3.5 *N*) hydrochloric acid in the distilling flask. During continual dropwise addition of more acid, 300 ml was distilled in 90 to 100 minutes. It will be shown later that this is satisfactory for most cases; for the time being relative values only are required. Fifty ml of water was then added to the distillate, and the furfural determination was carried out in the manner just described. When steam was used, the volume of condensate was 625 ± 40 ml. Since acid had been added in the same amount and manner as before, the acidities of the condensates varied, which necessitated titration of a portion with standard alkali. Weight-aliquots were then taken and sufficient concentrated hydrochloric acid added to give 350 ml, 2.7 *N* in HCl, after which the furfural determination was made as before.

The results of the distillations are listed in table 2 and show that the use of NaCl+steam produces higher "pentosan" values than the simple distillation in each case. On the basis of these results it seemed desirable to use a salt which is more soluble in the hot hydrochloric acid than sodium chloride. Accordingly, experiments were carried out in which 55 g of NH_4Cl instead of 20 g of NaCl was used, but which were the same in all other respects. The results are given in table 2

¹² Such a trap was recommended by Hughes and Acree, but was found to be superfluous in these pentosan distillations. In 12 distillations of material containing 11 to 19 percent of pentosans, corresponding to 0.1 to 0.17 g of furfural, never more than 0.1 mg and usually 0.1 mg of furfural was found in the trap. Since this corresponds to some 0.01 to 0.02 percent of pentosans, and is of the same order of magnitude as the experimental error, such corrections may be neglected. If the condensate in the receiver is warm, either because of too rapid distillation or inefficient cooling in the condenser, it is possible that the higher vapor pressure of furfural in the receiver may cause low results if a trap is not used. The temperature of all condensates in the present work was approximately 25° C.

and show that "pentosan" values in the distillations with NH_4Cl +steam are higher in every case than in the simple distillations or in those with NaCl +steam. Blank runs with the salts, but without the cellulose materials, showed negligible amounts of oxidizable substances, less than 0.05 percent expressed as pentosan, in the distillates.

TABLE 2.—Comparison of the "pentosan" values obtained by using various methods of distillation

Samples ^a	Type of distillation							
	Simple distillation		Sodium chloride with steam			Ammonium chloride with steam		
	"Pentosan" values		"Pentosan" values		Gain over simple (% pentosan)	"Pentosan" values		Gain over simple (% pentosan)
	Percent	Average	Percent	Average		Percent	Average	
<i>C</i> , new rag paper.....	$\left\{ \begin{array}{c} 0.7 \\ .8 \\ .7 \\ .7 \end{array} \right\}$	0.7	$\left\{ \begin{array}{c} 1.0 \\ 1.2 \\ 1.2 \end{array} \right\}$	1.1	0.4	$\left\{ \begin{array}{c} 2.1 \\ 1.8 \\ 2.1 \end{array} \right\}$	2.0	1.3
<i>E</i> , special sulfite pulp.....	$\left\{ \begin{array}{c} 2.9 \\ 2.8 \\ 2.9 \\ 3.0 \end{array} \right\}$	2.9	$\left\{ \begin{array}{c} 3.2 \\ 3.2 \\ 3.1 \end{array} \right\}$	3.2	0.3	$\left\{ \begin{array}{c} 4.2 \\ 4.6 \\ 3.7 \\ 4.2 \\ 4.9 \end{array} \right\}$	4.3	1.4
<i>F</i> , sulfite pulp.....	$\left\{ \begin{array}{c} 4.7 \\ 4.8 \\ 4.8 \end{array} \right\}$	4.8				$\left\{ \begin{array}{c} 6.1 \\ 6.4 \\ 6.3 \\ 5.8 \end{array} \right\}$	6.2	1.4
<i>I</i> , soda-sulfite (1:1) paper.....	$\left\{ \begin{array}{c} 11.2 \\ 11.0 \\ 11.0 \\ 11.0 \\ 10.9 \end{array} \right\}$	11.0	$\left\{ \begin{array}{c} 11.6 \\ 11.3 \end{array} \right\}$	11.4	0.4	$\left\{ \begin{array}{c} 12.8 \\ 12.6 \end{array} \right\}$	12.7	1.7
<i>H</i> , soda pulp.....	$\left\{ \begin{array}{c} 16.3 \\ 16.1 \\ 16.1 \end{array} \right\}$	16.2	$\left\{ \begin{array}{c} 16.9 \\ 16.3 \\ 16.8 \\ 16.4 \end{array} \right\}$	16.6	0.4	$\left\{ \begin{array}{c} 18.8 \\ 18.7 \\ 19.1 \\ 19.0 \\ 18.1 \\ 17.8 \end{array} \right\}$	18.6	2.4

^a The fiber contents of these samples, after correction for moisture, ash, and resin were, in the order listed, 0.92, 0.92, 0.91, 0.91, and 0.92 g, respectively.

The gains shown in column 6 are not of the magnitude to be expected if the distillations with NaCl +steam are instrumental in increasing the conversion of pentosans to furfural. Considering for the moment only the wood fibers, *E*, *I*, and *H*, the gain for sample *E* is 10 percent, whereas the gains for samples *I* and *H* are 3.6 and 2.5 percent, respectively. On the other hand, the gains correspond closely to those which would be expected if the distillation with NaCl +steam had the effect of increasing the yield of such unstable compounds as hydroxymethylfurfural, the amount of which is a function of the cellulose rather than of the pentosan content. This is further brought out by the results with the rag (cotton) sample *C*, where the percentage gain as a pentosan product would be very high, but as a cellulose product would be in good agreement with the other results.

These points are emphasized by the results obtained by using NH_4Cl +steam. The gains in volatile material, especially for samples *C*, *E*, and *F*, are obviously more related to the cellulose content (see footnote ^a of table 2) than to the "pentosan" content, which latter varied some sevenfold.

There is, however, another method of deciding upon the cause of the gain in volatile material shown in table 2. Kullgren and Tyden have shown that volatile material from glucose is completely destroyed upon redistillation, under conditions essentially those of the simple distillation, but with sodium chloride in the distilling flask. Furthermore, upon redistilling the distillate from a sulfite pulp, they found that volatile material corresponding to 1.1 percent of pentosan was destroyed, after applying a correction for losses of furfural. Since furfural can be distilled with small, fairly constant losses, as Kullgren and Tyden have found, any greater losses upon redistillation of the distillates must be ascribed to the decomposition of volatile material other than furfural.

The "simple" and the " NH_4Cl +steam" distillates from the two most common pulps, sulfite and soda, were subjected to repeated redistillation without steam or added salt. The distillates were weighed after each redistillation, and a weight-aliquot was taken for analysis. A small aliquot was also titrated with standard alkali for the purpose of determining how much hydrochloric acid and water were necessary to give the required acidity for analysis. The remainder was redistilled each time by adding 100 ml of it to the distilling flask, and allowing the rest to replace the distilling liquid by dropwise addition from the funnel. After the funnel was emptied in this manner, 110 ml of 12-percent hydrochloric acid was added dropwise and distillation continued until this also had been distilled. Thus, the volume of liquid in the distilling flask was always 100 ml. The final 110 ml of acid was shown by the work of Kullgren and Tyden to be necessary to complete the distillation of furfural.

The results of such repeated redistillations are given in table 3. The corrected values were calculated from the uncorrected values by taking into account the small losses of furfural itself during a distillation. This method of calculation, and the magnitude of the losses of furfural for the type of apparatus used, will be dealt with in the next section. The results, both corrected and uncorrected, show that large amounts of volatile material far less stable than furfural are contained in the original distillates from the pulps. This is especially true for the NH_4Cl + steam distillates. The results also show that after one or more redistillations the unstable volatile material has been destroyed, and an essentially unchanging amount of stable volatile material, presumably furfural, remains, irrespective of initial "pentosan" values.

This confirms the previous conclusion that the higher "pentosan" values, obtained by distilling from salt solutions in a current of steam, are due to an increased yield of a volatile material other than furfural, probably hydroxymethylfurfural, from cellulose.

It does not appear advisable, therefore, to replace the much simpler distillation now in general use in the pentosan determination by either the NaCl or NH_4Cl +steam procedures. Furthermore, the use of such salts to salt out the volatile reaction products in this or similar distillations should be followed by some method of identifying the components of the distillates. Kullgren and Tyden distinguished

between the volatile products by redistilling once, and a proposed method for the determination of pentosans¹³ has been based upon their procedure; but it is evident from table 3 that one such redistillation may not suffice for all cases.

TABLE 3.—Effect of redistillation of "pentosan" distillates

[Percentage of "pentosan." All redistillations by "simple" method]

Type of original distillation	Sulfite pulp, Sample F						
	Original distillate from pulp	First redistillation of distillate		Second redistillation of distillate		Third redistillation of distillate	
	Uncorrected average *	Uncorrected	Corrected average	Uncorrected	Corrected average	Uncorrected	Corrected average
Simple.....	4.8	{ 3.79 3.93 }	4.0	{ 3.73 3.88 }	4.0	{ 3.71 3.76 }	4.0
Ammonium chloride with steam.....	6.2	{ 4.16 4.16 4.33 4.20 }	4.3	{ 3.68 3.85 3.69 3.88 }	4.0	{ (3.27) 3.73 3.55 3.58 }	3.9
	Soda pulp, Sample H						
Simple.....	16.2	{ 15.45 15.38 }	15.8	{ 14.59 14.60 }	15.3	{ 14.25 14.34 }	15.4
Ammonium chloride with steam.....	18.6	{ 15.55 15.38 15.72 }	15.9	{ 15.17 14.62 14.81 }	15.6	{ 14.70 14.25 14.50 }	15.6
	Cotton rag paper, Sample C						
Simple.....	0.7	{ 0.37 .26 .30 }	0.3	{ 0.14 .33 .26 }	0.2	{ 0.23 .21 .20 }	0.2

* The average values in this column were taken from table 2.

The method used in this publication for calculating pentosan content is based upon the assumption of theoretical conversion of pentosans to furfural, and the expression is given in the last section. The methods of calculating pentosan content in use at the present time are based upon an assumed conversion of 80 percent, which is a purely arbitrary figure. It was never actually determined with pentosans, since no distillation with a pure pentosan has been reported but was taken as the approximate average of 88 and 74 percent, which are the observed percentage conversions to furfural of the respective pentoses, xylose and arabinose. Recently, Hughes and Acree reported 100-percent conversion of xylose to furfural, by use of the NaCl+ steam procedure. In the present work, it was found that neither this procedure nor one much more suitable for decreasing the decomposition of volatile material, NH_4Cl +steam, was found to increase significantly

¹³ Charles Doree, The Methods of Cellulose Chemistry, p. 367 (Chapman and Hall, Ltd. London, 1933).

the yield of furfural from pentosans. It appears, therefore, to be a sounder practice to assume a theoretical conversion of pentosans to furfural for the basis of calculation, since minimum pentosan content is thereby attained. As a minimum value, a pentosan content may have a definite significance.

The reproducibility of the method involving simple distillation is satisfactory. In applying this method to the routine analysis¹⁴ of 68 samples of pulps and papers at this Bureau, the average agreement between duplicates was 0.16 percent of pentosan. The duplicability of the methods employing steam distillation is affected by the variations in volume of steam passed. Such variations were difficult to control, which is reflected in the large variations in some of the results in table 2.

3. RECOVERY OF FURFURAL BY SIMPLE DISTILLATION

Known quantities of a standard solution of furfural were added to hydrochloric acid in the distilling flask, to make 100 ml of a solution, 12 percent by weight in hydrochloric acid. While continually adding more acid, 300 ml was distilled in 90 minutes in the simple distilling apparatus, after which 50 ml of water and 250 g of ice were added to the distillate, in which the furfural was then determined. The results given in table 4 show that the average loss in distilling amounts of furfural corresponding to the range of 4 to 19 percent of pentosan, is 3.1 percent of the furfural taken for distillation. This loss is somewhat lower than that found by Kullgren and Tyden, whose experiments, under similar conditions, showed a loss of 5 percent. They do not state, however, how the distillates were protected from air currents during the distillation, and the discrepancy can be explained by assuming that these workers used the usual method of allowing the distillate to drip from the condenser onto a paper filter held in a funnel. This is an ideal arrangement for causing volatilization of furfural, and was avoided in the present work.

TABLE 4.—*Loss of furfural during the simple distillation*

Series	Furfural taken for distillation *	Furfural found in distillate	Loss of furfural	Loss of furfural
	<i>Grams</i>	<i>Grams</i>	<i>Grams</i>	<i>Percent</i>
1.....	0.125 2	0.121 6	0.003 6	2.9
	.125 2	.121 5	.003 7	3.0
2.....	.100 1	.098 29	.001 8	1.8
	.100 1	.098 34	.001 8	1.8
3.....	.050 00	.048 91	.001 1	2.2
	.050 00	.048 60	.001 4	2.8
4.....	.024 96	.023 74	.001 2	4.8
	.024 96	.023 69	.001 3	5.2
Average.....				3.1

* The values in this column are the same as the average determined values in table 1, column 3.

As a matter of fact, however, high precision in the value of the correction is not necessary in the usual pentosan determination, because it has already been indicated that for a material containing 10 percent of pentosan any error in the amount of furfural is only one-tenth as large in terms of pentosan percentage.

¹⁴ Performed by C. I. Pope.

The pentosan values in table 2 were not corrected for losses in furfural, since the values evidently represent more than pentosans alone. This does not detract from their usefulness, however, since only relative values were needed.

The corrected values in table 3 were obtained by dividing the average uncorrected value by $(0.976)^n$, where n is the number of the redistillation, either 1, 2, or 3. The figure 0.976 corresponds to a recovery of 97.6 percent, or a loss of 2.4 percent, the average loss upon distilling quantities of furfural in the range 0.05 to 0.125 g of furfural. The average for this range, rather than the 3.1 average of table 4, was taken after it was observed that the use of the latter caused the values of table 3 to rise with succeeding distillations. This evidence, together with the fact that the percentage loss in the case of the smallest amount of furfural of table 4 is abnormally high, appears to warrant the omission of the latter from an average to be applied to redistillations from soda pulp, inasmuch as the amount of furfural involved therein, 0.10 g, is rather far removed from the smallest quantity of furfural listed in table 4. For the sulfite pulp, either average may be used without significant differences in individual values. To correct for furfural losses during a distillation from a pulp, however, the recovery may be taken as 0.97, since this is not raised to a higher exponential power, and leads to the approximate factor 1.03.

By applying this type of correction, the amount of furfural in the original distillate may be calculated from the subsequent redistillations. This is not strictly true for the first redistillation, since not all of the unstable volatile material had been destroyed at this point.

4. VOLATILE MATERIAL ARISING FROM CELLULOSE DURING THE SIMPLE DISTILLATION

The results in table 3 showed that volatile material from substances other than pentosans is included in the original "pentosan" distillates from common wood pulps, in the simple distillation procedure. By subtracting the values of the second or third redistillation from that of the original "simple" distillate, a difference of approximately 0.8 percent for both sulfite and soda pulps, calculated as a pentosan, is seen to represent the unstable volatile material which is not furfural. The value of 0.8 is a minimum, since the values for the last two redistillations may represent other stable volatile materials beside furfural. This value is in good agreement with that of 1.1 percent, obtained by Kullgren and Tyden using a sulfite pulp, inasmuch as these workers distilled from solutions of hydrochloric acid saturated with NaCl, which procedure yields greater quantities of unstable volatile material in the original distillate than the simple procedure used in the present work.

The value of 0.8 appears to be a correction which could be applied to the results of simple distillations of wood pulps, in order to arrive at a more nearly correct pentosan value. It would be desirable, however, to check this value by an independent method. This appears to be possible by studying the rate of the simple distillation beyond the first 300 ml, and then extending the rate data back through the first 300-ml period.

Accordingly, the distillation was subjected to further study. By continuing the addition of 12-percent hydrochloric acid and distillation beyond the first 300 ml on a group of materials derived from wood

and cotton, it was found that additional volatile material was obtained in all cases. In table 5 the roman numerals represent the distillate fractions. The calculations were carried out as though all volatile substances had arisen from pentosans. Under I are listed the initial values of the materials, obtained in the "simple" distillation of 300 ml in 90 to 100 min. The succeeding fractions were each 300 ml for the materials derived from cotton, and 150 ml for those derived from wood, distilled at the usual rate. The fractions were diluted to 350 ml with water and, whenever necessary, with hydrochloric acid before the addition of ice and bromate-bromide solution. Distillation of all samples beyond the first 300 ml was continued until the amount of volatile material per 150 ml of distillate became of the same order of magnitude as the experimental uncertainty.

The behavior of the wood pulps *D*, *E*, and *F*, beyond fraction I, and pulps *G* and *H* beyond fraction II, is in all cases so similar as to suggest that the volatile material in these fractions arose from the same source. The small differences between given fractions for the various materials are of the same order of magnitude as differences between given fractions of duplicate samples, not shown for the sake of clarity. Inasmuch as the amounts of cellulose present in the samples *D* to *H* were similar (see footnote *a* of table 5), as contrasted with the amounts of pentosans, it is very probable that the additional volatile material arose from the cellulose in the samples. On the other hand, it is extremely improbable that the fractions referred to represent pentosans, since that would require that the pentosan content of each material, regardless of its original value, should reach a common value, other than practically zero, after 300, 450, 600, etc., ml of distillate. Only in the case of the two pulps containing relatively large quantities of pentosans, samples *G* and *H*, does it appear that small quantities of pentosans, 0.2 percent, remain unconverted after 300 ml of distillate, and that even in these examples the fractions after II are essentially the same as the corresponding ones of the other pulps.

TABLE 5.—Results of continued "simple" distillation with HCl of cellulose materials from cotton and wood

(Expressed as percentage of pentosan *)
Distillate fractions: • I to VII=300 ml

Samples	I (Initial values)	II	III	IV	V	VI	VII
A, cotton ^b	0.57	0.67	0.45	0.33	0.20	0.16	0.11
B, new white rag (cotton) paper ^b66	.68	.49	.34	.20	.19	.12
C, new white rag (cotton) paper ^b75	.65	.47	.35	.21	.32	.11

Distillate fractions: • I=300 ml; II to VII=150 ml							
D, special sulfite pulp ^d	1.33	0.46	0.46	0.33	0.33	0.25	0.06
E, special sulfite pulp ^d	2.86	.44	.42	.40	.32	.14	.09
F, sulfite pulp.....	4.72	.44	.39	.33	.25	.19	.16
G, unbleached sulfate pulp ^b	8.44	.67	.42	.31	.20	.12	.08
H, soda pulp.....	16.05	.68	.46	.28	.24	.18	.13

* The calculations were based upon the weights of the 1-g samples, corrected for moisture, ash, and resin, which thereby became as follows for samples A to H, respectively: 0.93, 0.83, 0.92, 0.96, 0.92, 0.91, 0.87 and 0.92 g. Paper samples B and C were made from the same batch of cotton rags. Paper B contained 10 percent of clay filler. The expression used for the calculations is given in the section "Method in Detail," omitting the constant *c* in these instances.

^b These experiments were performed by C. I. Pope.

^c This material was highest quality sterilized cotton, such as is ordinarily used for surgical purposes.

^d These pulps had been subjected to modified chemical purifying processes by the manufacturers.

* The values for all fractions were corrected for the slight amount of volatile material arising from the rubber stoppers, which was found to be 0.02 percent per 150 ml of distillate, expressed as pentosans. This was found by distilling 300 ml of 12-percent hydrochloric acid alone in the apparatus.

The question now arises as to how much volatile material due to cellulose was obtained during the regular pentosan determinations in fraction I. This quantity could be estimated graphically from the values for the distillate fractions beyond I; or more simply, and sufficiently precisely for the present purpose, by selecting values which are compatible with those of the subsequent fractions. To do this, it is necessary to know something of the relative rates of evolution of volatile material by cellulose before and somewhat beyond the 300-ml point. That this rate is not greater before than after the 300-ml point is shown by the data for the cotton materials *A*, *B*, and *C*, in table 5, wherein the values for fractions I and II are essentially equal.

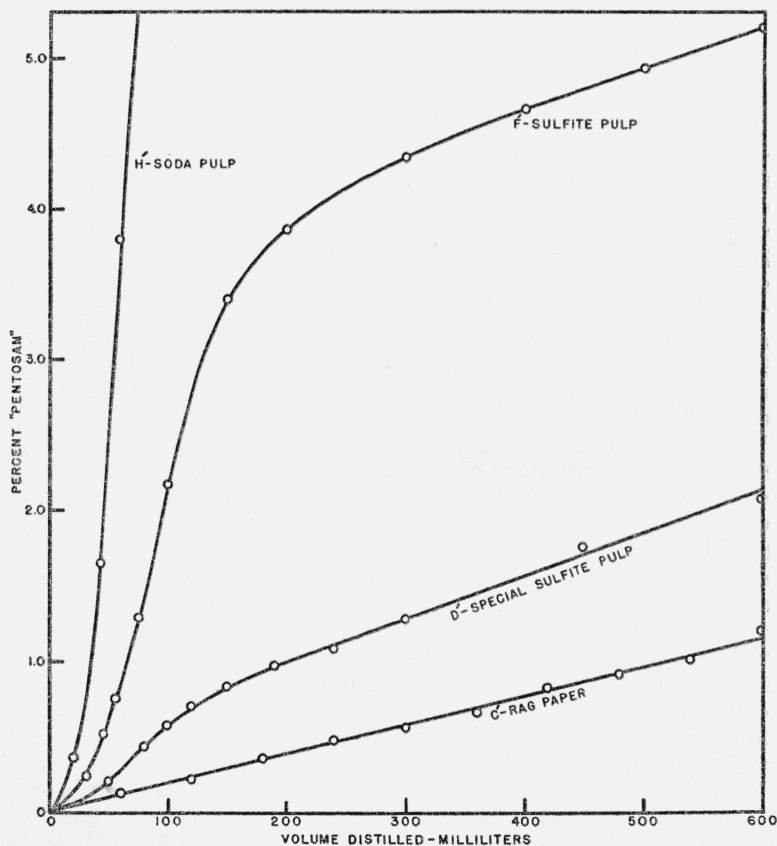


FIGURE 1.—Rate of evolution of volatile material.

A more detailed study of the "simple" distillation with sample *C* was made, again using a 1-g sample. The volatile material was determined in successive 60-ml fractions for the first 600 ml. The corresponding curve *C'* is shown in figure 1 and is best represented by a straight line. This shows definitely that the rate of evolution of volatile material from cellulose is not greater before than after the 300-ml point. A basis is thus established for assigning a maximum value of approximately 0.9 as the amount of volatile material due to

cellulose in the first distillates by the simple procedure, for samples *D*, *E*, and *F*. For samples *G* and *H* this value would be higher if only fraction II were considered. As previously mentioned, however, fraction II for samples *G* and *H* appears to be abnormally high because of small amounts of residual pentosans, since beyond II the distillate fractions for samples *G* and *H* resemble closely the corresponding fractions for samples *D*, *E*, and *F*. Thus, 0.9 appears to be the maximum value for all of these materials.

The maximum value of 0.9 is in good agreement with the minimum value of 0.8 previously arrived at in another manner. There is, however, evidence available that 0.9 is also a most probable value from the standpoint of the reasoning just employed. In the study of reaction rates in general, a straight line usually indicates that only one substance is reacting with the medium—in this case, hydrochloric acid. This is especially true where large differences in the amounts of two possibly reactive materials, polyoses and pentosans, are known to exist. By the method of redistillation of the distillate from sample *C*, table 3, shows that most of the original distillate was not furfural. Even if it could be shown that the small amount of stable volatile material in the third redistillation of sample *C*, table 3, were furfural, there still remains the possibility that such a small amount of furfural could arise from the decomposition of hydroxymethylfurfural, as several workers report.¹⁵ Thus, the most probable assumption is that curve *C'* is due to cellulose, and that the rate of evolution of volatile material by cellulose is essentially equal before and somewhat beyond the 300-ml point. This assumption does not rule out less probable possibilities, but furnishes a measure of substantiation of the value of the correction 0.9, already fixed by limits.

The correction 0.9 refers to the cellulose in the fibrous materials studied, and is apparently not affected by wide differences in the small amounts of other materials present, such as resin,¹⁶ lignin, wax, etc., known to exist in these types of pulps. Furthermore, the cellulose itself had been subjected to widely different treatments in the normal preparation of these pulps, without affecting this behavior of the cellulose. Since, moreover, the pulps studied were representative of the usual papermaking materials, it appears that the correction is generally applicable to like distillations of such commercial materials.

It was deemed of interest to continue the detailed rate studies of the other pulps listed in table 5. An entirely different type of curve was obtained with the special sulfite pulp *D*. For the first 180 ml, curve *D'* resembles in type curves *F'* and *H'*,¹⁷ especially in that the maximum rate, corresponding to the maximum slope, appears at about the same part, 75 ml, of all three curves, which apparently is characteristic of pentosans. From 180 to 600 ml, curve *D'* is very

¹⁵ Kirmayer, Chem.-Ztg. **19**, 1003 (1895). Erdmann, Ber deut. chem. Ges. **43**, 2391 (1910).

¹⁶ Glue, starch, and casein, often present in papers, were found to give rise to volatile material not exceeding 0.04 percent, calculated as a pentosan. This was determined by distilling quantities of these materials corresponding to the high glue, starch, or casein contents of 4 percent, based upon the weight of the paper, alone with hydrochloric acid as usual and then analyzing with bromate-bromide, etc., by the usual method.

¹⁷ The remainder of curve *H'* was omitted for convenience. It can be reconstructed, if desired, from the following rate data for curve *H'*:

Volume distilled: ml	Pentosan %	Volume distilled—Continued. ml	Pentosan %
20.....	0.36	150.....	12.49
40.....	1.65	180.....	14.29
60.....	3.80	220.....	15.09
80.....	6.10	320.....	15.94
100.....	8.74	420.....	16.39
120.....	10.65	520.....	16.74

similar to C' , and in this region the volatile material in both cases apparently arose from cellulose. The slope of the latter part of D' is 1.6 times that of C' , which probably represents the difference in the rates of hydrolysis of the two types of cellulose. If it may be assumed that the cellulose in cotton is more resistant to hydrolysis than that in wood pulps, under the conditions of distillation, as it has been found to be in highly concentrated, 41-percent hydrochloric acid,¹⁸ it is seen that hydrolysis, or another similar reaction, is a necessary preliminary step in the production of volatile material from cellulose. Finally, it is seen from figure 1 that the slope of the straight portion of curve F'' is the same as that of D' , which is to be expected if the same type of cellulose is here producing the volatile material.

The straight line, occurring before the 600-ml point is reached, appears to be characteristic of cellulose, and is the type of curve to be expected as long as the available reactive surface does not change appreciably in area. Beyond 600 ml. the reactive area apparently diminishes rapidly as the fibers start to disintegrate and disappear, after which the rates of production of glucose, and consequently of the volatile material, decrease, and the curve approaches a limiting value.

Small amounts of methylfurfural are probably also obtained from the methylpentosans during the regular determination. This may be distinguished from furfural, when these two are present alone,¹⁹ but in distillates from cellulose materials the presence of hydroxymethylfurfural makes the direct application of the method uncertain. This does not matter for the present purpose, since the method is intended for the determination of pentosans as a group, as distinguished from cellulose.

III. METHOD IN DETAIL

In view of the results obtained in this study, the following method is recommended for the determination of the pentosan content of pulps and papers.

Approximately 1 g of the ground material is taken for analysis. The distillation is performed in a 500-ml distilling flask, above which is mounted a separatory funnel containing 400 ml of 12-percent hydrochloric acid. Rubber stoppers may be used if desired. One hundred milliliters of the acid is added to the sample from the separatory funnel and the remaining 300 ml is added dropwise as rapidly as necessary to maintain the volume in the distilling flask at 100 ml. A water-cooled condenser delivers through an adapter into a 1-liter glass-stoppered reagent bottle. The time of distillation is 100 minutes, during which time 300 ml is distilled. It is important to observe the requirements of time and quantity.

Fifty milliliters of water and approximately 250 g of crushed ice²⁰ are added to the distillate. After the temperature has fallen to -2° to 0° C, 20.00 ml of 0.2 *N* bromate-bromide solution²¹ is introduced with a minimum of agitation, after which the reagent bottle is closed and shaken well. After 5 minutes, 10 ml of a 10-percent solution of

¹⁸ E. C. Sherrard and A. W. Froehke, *J. Am. Chem. Soc.* **45**, 1729 (1923).

¹⁹ Elizabeth E. Hughes and S. F. Acree, *Ind. Eng. Chem., Anal. Ed.* **9**, 318 (1937).

²⁰ The ice should be relatively pure, although this is not essential, as some of the same ice is used in the blank determinations.

²¹ Contains 5.57 g of KBrO_3 and 50 g of KBr , both of reagent grade, per liter.

potassium iodide is added. After again shaking the bottle thoroughly to allow absorption of the bromine vapors, the free iodine is titrated with 0.1 *N* sodium thiosulfate solution, using starch indicator.

The blank is determined by diluting 270 ml of 12-percent (3.5 *N*) hydrochloric acid to a volume of 350 ml, adding ice, bromate-bromide, and potassium iodide in the usual manner, and titrating with 0.1 *N* thiosulfate solution.

The pentosan content of wood pulps and papers made from wood pulps is calculated by substitution in the following expression:

$$\text{Pentosans, percent} = 1.03 \left[\frac{6.60 \times N \times (v_2 - v_1)}{W} \right] - C$$

C = volatile material arising from cellulose during the simple distillation. It has the value 0.9 for 300 ml of distillate.

N = normality of thiosulfate solution.

*v*₂ = blank on bromate-bromide solution under test conditions.

*v*₁ = volume of thiosulfate solution necessary to titrate the solution after oxidation.

W = weight of the test specimen after correcting for moisture, ash, resin, glue, and starch.

The factor of 1.03 is the correction necessary to account for the loss of furfural during the distillation from a pulp. This loss was taken as approximately 3 percent, based upon the average loss occurring in distillations of the usual amounts of furfural.

The factor 6.60 is the product of $100 \times 0.0480 \div 0.727$, in which 0.0480 is the weight of furfural in grams corresponding to 1 ml of *N* thiosulfate solution, and 0.727 is the theoretical conversion factor of pentosans to furfural. If the analyst desires values which are comparable with those used in Kröber's tables, in which the conversion of pentosans to furfural is arbitrarily assumed to be 80 percent, for which the conversion factor is 0.582, the following expression may be used, disregarding the furfural and the cellulose corrections:

$$\text{Pentosan content, percent} = \frac{8.25 \times N \times (v_2 - v_1)}{W}$$

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